Variations of parameters in nucleation process under different external conditions

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Abstract

The nucleation process under different external conditions is considered. It is shown that the duration of this process can be connected with the microscopic corrections to the free energy of the critical embryo. Connection between variations in the value of the critical embryo free energy and the duration of the nucleation stage is given for several types of external conditions. This connection is in some cases reciprocal to uncertainty relation in quantum theory. In Appendix the derivation of main features of the general theory on the base of restrictions coming from the possibility of effective and stable observations is given.

1 Introduction

The first order phase transitions are usually studied at example of the transition of the supersaturated vapor into a liquid state. This example allows to go away from the numerous parameters characterizing the state of the mother phase and the state of the new phase. But even in this case there is no perfect coincidence between theoretical predictions and results of experiments. Now it is clear that the stationary rate of nucleation is determined with a bad accuracy and there are serious physical reasons lying behind this

problem. So, one can speak about some uncertainty in determination of the stationary flow of embryos or of the stationary rate of nucleation. The bad accuracy can be caused by two main reasons

- The absence of the real stationary conditions for nucleation.
- The bad value of the free energy of the critical embryo. This value is included in the formula for the stationary rate of nucleation.

It is clear that according to [1] the transition of the embryos from the pre-critical zone to the post-critical can occur far from the position of the critical embryo and, thus, the formula for the stationary rate of nucleation has to be reconsidered. But this case is rather rare and here we shall consider situations when the transition from the pre-critical zone to the post-critical zone goes through the critical point, i.e. through the position of the critical embryo.

The numerous investigations of the establishing of the stationary state in the near-critical region showed that the situation where the stationary state is not established are very rare also. To see such situations one has to cut off the power of metatstability practically immediately after the moment when this metastability was created. So, this opportunity is also out of consideration here.

The paper is organized as following: In the next section the situation with the artificial cut-off of the supersaturation is analyzed. Then the situation of decay of metastable phase is considered. Here the form of relation connecting the variations of parameters of the process resembles the uncertainty relations in quantum mechanics. That's why in appendix the derivation of the basic characteristics of the calssical mechanics and quantum theory including the uncertaity relations is given. The last situation which is considered is the external conditions of graduate creation of metastability in the system. Here the form of relations connecting the same parameters of the process radically differs from those in the previous situation.

2 Determination of the pure rate of nucleation

The stationary rate of nucleation in the main order has rather transparent origin - the rate of nucleation is proportional to exponent of the free energy G

of the critical energy taken in thermal units. Here and later all values having the sense of energy are taken in thermal units kT, where k is the Bolztman's constant and T is the absolute temperature.

Determination of the free energy G is a very complex procedure. The problem is that the critical embryo has a number of molecules ν_c big enough to make useless all calculations based on dynamic laws of motion. On the other hand the number ν_c is not big enough to apply the laws of statistical mechanics. But since there is no alternative one has to use the approach of thermodynamic description.

Unfortunately the situation is more dramatic because one has to calculate the exponent of the free energy. Although the relative error in determination of the free energy becomes small the exponent reflects the absolute errors and these errors are not small even with $\nu_c \to \infty$.

Really, the extraction of a separate embryo from the whole system is some simplification. It works satisfactory because the intensity of exchange between the embryo and environment is much more weak than the intensity of relaxation in the embryo to the state of internal equilibrium

$$t_{int} \ll t_{ch}$$

where t_{int} is the time of internal relaxation and t_{ch} is the characteristic time of exchange with environment. But here appears a problem - it is impossible to determine concretely the type of conservation equations for the separation of the embryo. So, it is impossible to determine the ensemble in statistical mechanics.

From the first point of view there is no problem because different ensembles in statistical mechanics give equivalent results. But this means only that the relative values of macroscopic variables are equivalent. More precisely the relative difference of values have the order of $\ln n/n$ where n is a number of particles in the system. Taking exponent one can see the difference in n times.

Also one has to take into account the possibility of fluctuations which gives for the thermodynamic potential the shift of the order $n^{1/2}/n$ i.e. $n^{-1/2}$. So, the exponent will have the correction in $\exp(\sim n^{1/2})$ times. This correction is enormously big. Certainly, one can say that fluctuations are already taken into account but the trace of incompleteness of the theoretical derivation still remains.

The next source of inevitable difficulties is the limitations on the size of the embryo. There are two aspects of this problem

- Since the system has a finite dimension the continuous spectrum of the energy transforms into the discrete energy levels and all integrations have to be replaced by summations. It is vary hard to do because the Euler-Maclaurin's decomposition is not converging one, but only asymptotic and the formal transformation here is not possible.

- There appear the simple geometric problems like the difference between position of the surface of tension and the equimolecular surface. The conception of the surface of the embryo which is necessary to write the term with the surface energy and the equation of the material balance. But positions of surfaces do not coincide. This leads to the additional term of the order of $n^{1/3}$.

Following the second item we shall write the formula for the free energy as

$$G = -b\nu + a\nu^{2/3} + c\nu^{1/3}$$

where parameters a, b, c have a simple physical meaning: b is the difference of chemical potentials in a mother and a new phase, a is the renormalized surface tension, c is connected with the difference between equimolecular surface and the surface of tension at the plane surface. Later there appear corrections due to the curvature of the surface and it is convenient to continue this decomposition writing it as

$$G = -b\nu + a\nu^{2/3} + \sum_{i=-1}^{\infty} c_i \nu^{-i/3}$$

The term with $i = 0$ looks like $const + c_0 \ln \nu$ and it is connected with non-equivalence of ensembles.

As the result of all these constructions one can state that there is a microscopic addition δG to the value of G_0, there is also an addition $\delta\nu_c$ to the argument of maximum ν_{c0}. Here the values with a subscript 0 are the values based on the capillary approach, i.e. on

$$G = -b\nu + a\nu^{2/3}$$

The experiments intended to get the rate of nucleation and the free energy of the critical embryo are ordinary constructed in a following manner: At the initial moment of time there is a metastable state with no embryos of the new phase. After some time t_{cut} the metastability in the system is artificially

diminished to forbid the formation of new embryos. Then the number of droplets will be

$$N = Jt_{cut}$$

Here no depletion of the vapor phase is taken into account. To neglect the depletion of the mother phase it is necessary to fulfill

$$t_{cut} < t_{depl}$$

where t_{depl} is the time of depletion, which will be determined in the next section. Then here

$$\delta t = 0$$

and

$$\delta N = (\exp(\delta G) - 1)N_0$$

For very small δG one can linearize the exponent and get

$$\delta N = \delta G N_0$$

3 Decay of metastable state

Now we shall consider the process of the mother phase depletion. To give quantitative estimates it is necessary to specify the rate of the droplets growth. For the supercritical embryos, i.e. for the droplets it is reasonable to adopt the free molecular regime of growth. Under this regime the question of profile of the mother phase around the droplet can be solved extremely simple - there is no such a profile and, thus, the mother phase depletion can be described in a very simple manner.

Under the free molecular regime of growth the number of molecules inside the droplet grows as

$$\frac{d\nu^{1/3}}{dt} = \zeta/\tau$$

where ζ is the supersaturation of the mother phase and τ is some characteristic time which is approximately a constant value.

Then the number of molecules inside the new phase will be

$$Q = \int_0^t J(t')\nu(t')dt'$$

where $\nu(t')$ is the number of molecules inside the droplet formed at t'.

The rate of nucleation is connected with the distribution function f over $\rho = \nu^{1/3}$ by

$$f = J\tau/\zeta$$

Then

$$Q = \int_0^z f(z)(z-x)^3 dx$$

One can show that the depletion occurs in a very rapid avalanche manner. Before the essential depletion one can consider f as a constant f_* at the beginning of the process and get

$$Q = f_* z^4/4$$

The length of the spectrum is determined by the following condition

$$Q = \frac{\zeta}{\Gamma}$$

where

$$\Gamma = -\zeta \frac{dG(\nu_c)}{d\zeta}$$

Then

$$f_* z^4 = \frac{4\zeta}{\Gamma}$$

and one can determine the time t_{depl} from the following condition

$$J_* \frac{\tau}{\zeta} t_{depl}^4 (\frac{\zeta}{\tau})^4 = \frac{4\zeta}{\Gamma}$$

where

$$J_* = f_* \zeta/\tau$$

Having written J as $Z\exp(-G(\nu_c))$ where Z is the Zel'dovich' factor one can come to

$$Z\exp(-G) t_{depl}^4 (\frac{\zeta}{\tau})^3 = \frac{4\zeta}{\Gamma}$$

The last equation allows the analysis of variations of the time on depletion and the free energy of the critical embryo formation.

Having inverted variations one can get

$$Z\exp(-G-\delta G)(t_{depl}+\delta t)^3 (\frac{\zeta}{\tau})^4 = \frac{4\zeta}{\Gamma}$$

This is the final equation and one can see that the total number of droplets can be calculated as

$$N = J_* t_{depl}$$

In the main order

$$N \sim \exp(-3G/4)$$

and

$$\delta N \sim N_0(\exp(-3\delta G/4) - 1)$$

The equation on δG, δt can be linearized which gives

$$\frac{\delta t}{\delta G} = \frac{t_{depl}}{4}$$

This equation is reciprocal in its functional form to the uncertainty relation in quantum mechanics

$$\delta E \delta t = const$$

which combines the uncertainty in energy E and in time t. That's why in Appendix the method based on uncertainty relation is presented. It is necessary to stress that the derivation in appendix has a special meaning and demonstrates some new features.

4 Gradual creation of a supersaturation

Ordinary the external conditions have a continuous slowly varying character. Then one can introduce the ideal supersaturation Φ, i.e. a supersaturation which would be in the system in the absence of formation of a new phase. Thus, the ideal supersaturation is fully governed by external conditions. At the variations of Φ of a relative order of Γ^{-1}

$$\delta\Phi = \Gamma^{-1}\Phi$$

the behavior of Φ can be linearized

$$\Phi(t) = \Phi_* + \frac{d\Phi}{dt}(t - t_*)$$

Here $*$ marks values at some characteristic moment.

The duration of the nucleation period is approximately $2t_{nuc}$ where t_{nuc} satisfies the evident relation

$$t_{nuc}\frac{d\Phi}{dt}|_* = \zeta_*\Gamma_*^{-1}$$

So, the value of t_{nuc} is absolutely independent on δG and, thus,

$$\delta t_{nuc} = 0$$

The moment t_* has to be chosen as the moment of the maximal intensity of the droplets formation, i.e. here as th moment of the maximal supersaturation. Then here

$$\frac{d\zeta}{dt} = 0$$

and

$$\frac{dQ}{dt} = \frac{d\Phi}{dt}$$

The variation δG certainly exists, but does it take place the variation of G_*? To see this variation one has to write the condition for the maximum of the supersaturation

$$\int_{-\infty}^{t_*} J_* \exp(\Gamma\frac{d\Phi}{dt}|_*(t'-t_*))\frac{\tau}{\zeta}\rho(t')^2\frac{3\zeta}{\tau} = \frac{d\Phi}{dt}|_*$$

One can get J_* outside of the integral and see that the previous equation reduces to

$$J_* = slow \quad function \approx const$$

It means that J_* is invariant. When we add to G some addition δG nothing will be changed. Simply the moment t_* will be attained earlier or later. Then it is possible to introduce a shift of t_* and this shift will depend on δG.

As the result one can state that in this case there is no variations of parameters δG_*, δt.

5 Conclusion

Having analyzed three concrete situations one can see that only in the situation of decay there is a variations of parameters and these parameters forms the relation reciprocal to uncertainty relation in quantum theory.

A The role of restrictions coming from the possibility of stable and effective calculations

At first the aim of this review was to show the role of requirements coming from the possibility of correct calculations in physics. Later the constructions based on the requirement to produce the stable calculations of the characteristics of the system gave some more general conclusions presented below.

We start from the general point of view and instead of concrete physical theory we consider the general qualitative causal theory based on the differential formalism. It is necessary to clarify the last sentence. When we mention "the differential formalism" it means that the theory uses the standard formalism of the differential calculation. The term "causal" shows that some events are considered as "reasons" of other events described as "sequences".

There is no other special assumptions to start our constructions, but later some rather evident notations will be made to give us the possibility to present concrete results.

A.1 Causality and time

It is necessary to introduce a variable (or a characteristic) to describe the property of causality. Really, our style of thinking is principally a causal style. But the qualitative formalism has to show what event is a reason and what event is a consequence. In everyday speech we use the terms "earlier" for the reasons and "later" for the consequences. For example, consider the number of cars and the number of crushes. It is clear and mathematical statistics can show that the number of crushes correlates with the number of cars. But what is the reason - the big number of cars or the big number of collisions? Mathematical statistics can not give us the answer. It attracts our attention only to the fact the the increase of cars is associated with the increase of collisions. Certainly, we know that the increase of the cars is the reason of collisions (However, collisions are in some sense the source of beaten cars and leads to increase of the total amount of cars, but beaten cars are excluded from consideration). But how it can be proven? Only by the fact the the increase of the number of cars occurs slightly earlier than

the increase of the number of collisions. In real macroscopic social systems one can not really observe this effect obviously and this produces additional difficulties. But our style of thinking is to search the reason and the reason is marked by the word "earlier".

It is quite possible to see the system where the number of collisions is the reason of the number of cars. Really consider the social or biological system where "collisions" are "sexual relations" and the role of cars is played by males and females. Then the opposite casual construction takes place. The number of collisions is the source of the number of males and females. And here one can say that collisions occurs earlier than the increase of the population.

The straight result of the given example is the necessity to introduce the the characteristic responsible for the casuality. This characteristic is called as the "time". It will be marked by a letter t. The task of the theory which is going to be constructed is to determine the dependence of characteristic of the system x on t, i.e. $x(t)$. If there are several characteristics $x_{(i)}$ of the system which are marked by the index i one can consider a vector $\vec{x}$. At first we shall consider the case of one variable x.

One can argue whether t is discrete or continuous. The arguments to consider discrete time t are connected with a quantum Zenon effect. To use advantages of the differential formalism we consider here t as continuous variable, at least at some first steps of our considerations. The interval for time will be $[a, b]$. Sometimes we shall take it as an interval $[-1, 1]$.

Here we have to state that the reversibility ordinary announced in the classical mechanics has absolutely another rather local sense. To see the formal reversibility one has to change all velocities and the there is no concrete method how to do this. So, this reversibility is only imaginary property. In a real world there is no way to change the direction of time. Time is the characteristic responsible for the causal relations in our world.

A.2 Properties of proximity

The function $x(t)$ has to be established by the theory and then it has to be checked by some experimental measurements. The measurement of x at the moment t_i will be marked x_i. Certainly, there is a characteristic error δt of the choice of the time moment. At the accurate measurements this error becomes infinitely small. Then to have an infinitely small error of x it is

necessary that $x(t)$ has to be a continuous function

$$x(t) \in C_{[a,b]}$$

Here we have to choose the measure of proximity. According to the central limit theorem of the probability theory the distribution of errors of stochastic variable (let it be y) under some rather wide spread conditions goes to the normal distribution N

$$N \sim \exp(-\alpha^2(y-\bar{y})^2)$$

where $\bar{y}$ is the mean value of y and α is some constant.

The last relation leads to the choice as the most appropriate metrics the ordinary metrics

$$||\vec{x}|| = \sqrt{\sum_{i=1}^{n} x_{(i)}^2}$$

This metrics corresponds to the scalar product

$$< x, y >= \sum_{i=1}^{n} x_{(i)} y_{(i)}$$

The last scalar product corresponds to the Pyphagorean theorem for orthogonal basis

$$\alpha_i^2 x_{(i)}^2 + \alpha_j^2 x_{(j)}^2 = x_{(ij)}^2$$

where

$$\alpha_i \vec{x_{(i)}} + \alpha_j \vec{x_{(j)}} = \vec{x_{(ij)}}$$

is treated as a vector sum and α_i, α_i are some constants. It is necessary to stress that $\vec{x_{(ij)}}$ will be orthogonal to all $\vec{x_{(k)}}$ with $k \neq i, j$ and the given property can be used again and again.

The necessity to use this property for our construction is the following. We have to stress that we do not know the "true" characteristics of the system. We can miss some of them. There is possible to see the situation when instead of a pair coordinates we take one coordinate which is a linear combination of the initial ones. But the form of the normal distribution N has to be the same as it stated by the central limit theorem. It is possible only when we take the mentioned scalar product.

Really, for the probability of two independent characteristics $x_{(i)}$ and $x_{(j)}$ we have

$$P = P_i P_j = \exp(-\alpha_i^2 x_{(i)}^2) \exp(-\alpha_j^2 x_{(j)}^2) = \exp(-x_{(ij)}^2)$$

Here we count $x_{(i)}$, $x_{(j)}$ from their mean values.

A.3 Dimensionality of a physical space

On the base of measurements we have to reconstruct the function $x(t)$. Consider the simplest case which is the case of one material point, i.e. a simplest system without any external ad internal parameters and characteristics. How many coordinates is necessary to introduce in order to describe this system? The evident answer is that the simplest case is one coordinate. But this answer has one disadvantage which will be considered below.

Suppose that $x(t)$ is some signal which is governed by stochastic process of random motion. The results of Poia [2] show that for the stochastic walking the return back to origin with the probability 1 will be infinitely many times when the dimension of space d is $d = 1$ or $d = 2$. When $d = 3$ or greater then the probability of the infinite number of returns is 0.

The illustration of these results can be easily seen if we mention that the diffusion equation corresponding to this process has the Green function with essential part

$$G \sim \exp(-\sum_i x^2_{(i)}/4D_{(i)}t)$$

where $D_{(i)}$ is corresponding diffusion coefficient. The rest in G is the normalizing factor depending only on t.

We see that the functional form of G does not depend on the number of the spatial variables. Here lies one of the possible reasons why we see the diffusion process clearly. This functional form coincides with the functional form of the normal distribution. Again this form is the exponential of the square form of the variables. This allows to speak about the distributions of this form as the result of the random walking process and the fundamental functional form which will be used below. Again one can see the invariant character towards the choice of the variables or their ignorance.

Now we have to describe the consequences of these results for the problem under consideration. When $d = 1; 2$ the infinite number of returns allows to construct the infinite set of measurements at the moments of these returns and have all measurements as the zero values. So, the trace of the random walks disappears. This effect is unsatisfactory and we need to have $d = 3$ or greater to exclude this effect.

Since there is no other characteristics of the material point there is no other candidates for the true dimension of the space and we have to admit that namely $d = 3$ is the crucial dimension.

A.4 Reconstruction of functional dependencies

The number of measurements of trajectory $\vec{x}(t)$ is a big finite number going to infinity. On the base of these measurements one has to reconstruct the functional form $x(t)$ (here it is sufficient to consider one variable). Since there are only two arithmetical operations (addition and multiplication) one can not go outside polynomials. Actually only polynomials can be constructed and calculated. All other functions which are ordinary used like sin, cos are no more than idealized infinite series of polynomials.

We have to restrict the class of functional dependencies allowed for $x(t)$. Really, for discontinuous functions one has to measure $x(t)$ at every point t which is certainly impossible. So, the consideration of the class of continuous functions is preferable not only from the physical point of view but also from the enormous expenditures of measuring. Fortunately according to the Weierstrass theorem every continuous function f at $[a, b]$ can be approximated by polynomial P

$$||f - P||_{C_{[a,b]}} < \epsilon \to 0$$

or

$$max_{a<x<b}|f - P| < \epsilon \to 0$$

The simplest form of approximation is interpolation. The property of interpolation means that having measured n times at moments $t_i, i = 1..n$ the function $x(t)$ we get $x_i = x(t_i)$ and the polynomial L has a property $L(t_i) = x_i$. Certainly, it is possible to construct the polynomial of a power $n - 1$ in a unique form.

But here one faces with the "no go theorem" which states that for every manner of the choice of interpolation nodes there exists a function which can not be interpolated [3]. Namely, the difference between function f and interpolation polynomial L has the estimate

$$||f - L||_C = O(\ln n)$$

where n is the number of nodes.

There exist recipes of Feier and Valle-Poussin [3] which allow to approximate f in C, but these recipes have no property of interpolation: there exist nodes where $P(t_i) \neq x_i$. So, we came to a strange situation with a trajectory which does not satisfy the results of measurements. Some analogy takes place in quantum mechanics.

Having started from the classical point of view we have to require that all measurements have to be satisfied precisely.

It is not a accidental coincidence that in the method of Valle-Poussin the approximated function does not coincide with the measurements at the half of points. This number can be hardly decreased because the weight used in this method is the optimal choice [3].

We come to a strange conclusion that at least some measurements can not precisely define the investigated dependence. This can be explained by impossibility of the fully precise determination in experiments of all possible characteristics of the system. In quantum mechanics this effect is called as "uncertainty relations".

A.5 Restriction of possible trajectories

The possible evident answer to solve the problems leading to a classical mechanics appeared from the "no go" theorem is to consider instead of the space $C_{[a,b]}$ the space of functions with restricted first derivative. For such functions one can see [4] that for every t

$$|x(t) - L(t)| \leq O(\ln n/n)$$

where n is the number of nodes (the number of measurements). Here the nodes are the Chebyshev's ones. The interval is $[-1, 1]$. So, here the interpolation procedure approximates the real trajectory. Now the (infinite) set of measurements can give us the form of trajectory.

There appeared two important consequences:

- There appeared a new auxiliary characteristic of the system - the velocity v or the momentum p. Now the description has to take into account this characteristic explicitly.

- The velocity of trajectory is limited by some constant c. This corresponds to the requirement of the special theory of relativity. So, one can assume that the special theory of relativity goes from this very simple restriction of the class of trajectories in order to have the convergence in procedure of interpolation.

As the special result we come to a conclusion that the trajectory and the first derivative of trajectory are the basic characteristics in description of the state of the system (or of the particle).

One has to stress that p or v can not be considered as the variables fully equivalent to coordinate x. In classical mechanics there exists a picture of Hamilton where x and p are formally considered as a pair of coordinates. But one has to remember that initially x and p have different senses and x is the main variable, while p is additional one. In consideration presented here it appeared as the characteristic only because the restriction of the class of trajectories.

A.6 The configuration space and the phase space

At first it is necessary to recall that there exists a simple style to present the state of a complex system - the configuration space and the phase space.

The configuration space is a space R^n where n is a number of coordinates of all particles in a system. The state of the system is a point in configuration space. The coordinates in configuration space are orthogonal and this is one of essential features in the future analysis. This orthogonality is an evident consequence of the simple fact that if different particles in the system are independent then the space is simply reduced to the sum of two configuration subspaces for particles (Certainly, the configuration space for a free material point is R^3). We assume this fact at least for negligibly interacting parts of the complex system.

When we add the momenta as auxiliary characteristics of the system we get the space R^{2n} of all coordinates and momenta of the system. Here also orthogonality takes place. One can say that this is simply the property of a linear orthogonal space or one can seek something behind this fact.

The problem which appears for every theory is that one does not know the number of coordinates of the system. The simplest structure of the physical construction implies that we have a system with the given number of interacting balls. They are referred as "particles". Certainly, one can not state that these particles are the simplest systems, they also have to be considered as complexes with rather complicated structure. In the field models the number of degrees of freedom is principally unknown. So, our approach has to allow the generalization to unknown coordinates, it has to manifest some invariance for the squeezing and for the developing of description. In approach to construct the field theories by continual integration procedure it is also necessary that the kernel has to be invariant for the arbitrary choice of the number of coordinates [5].

The subspace responsible for internal degrees of freedom has to be sep-

arated in some sense from the subspace responsible for external degrees of freedom. The best way to ensure this property is to consider these subspaces as orthogonal ones. The property of orthogonality is associated with the Pythagorean theorem

$$c^2 = a^2 + b^2$$

and with Euclidean postulate that at the given point one can put only one parallel line to the given line. This postulate leads to precise recipe resulting in the unique geometric operation. Then this postulate can be considered as reflection in the everyday life of intention to construct quantitative theory describing the world.

What functions satisfy the requirements put here? It is easy to see that only the square forms of characteristics (coordinates) allow the operation of squeezing. Really, for

$$F = \sum a_{(i)} x_{(i)}^2$$

with some constants $a_{(i)}$ if we miss some $x_{(i)}$ the functional form remain the same and is instead of $x_{(j)}, x_{(k)}$ we take a linear combination $x_l = b_j x_{(j)} + b_k x_{(k)}$ the form will be the invariant also.

Certainly, the square form can be reduced to the sums of squares by a linear transformation.

A.7 Classical motion

The knowledge of the function $x(t)$ means that we know the functional form for $x(t)$ which can be written as

$$H(x(\tilde{t}), t) = const$$

for some function H, where $\tilde{t}$ means that all preceding times are involved in description. The function H is called an "energy" or having written as a formula it is called the "hamiltonian". Giving more detailed description at the current moment t we can indicate the derivatives of trajectory

$$H(x, dx/dt, d^2x/dt^2, ..., t) = const$$

Since we have established that only the value $x(t)$ and the value of the first derivative $dx(t)/dt$ are included into description then we have

$$H(x, dx/dt, t) = const$$

The explicit dependence on time has to be excluded since all behavior of the system has to be invariant in respect to $t - t_0$ where t_0 is the time of preparation of initial state. Then we get

$$H(x, dx/dt) = const$$

For the dependence on $v = dx/dt$ since as it has been mentioned v is a formal auxiliary characteristic we have to take the formal square functional dependence as it is prescribed above

$$H(x, v) = U(x) + mv^2/2$$

where U is some function and $m/2$ plays the role of $a_{(i)}$

The requirement $H = const$ or $dH/dt = 0$ leads to

$$mdv/dt = -\frac{\partial U}{\partial x}$$

which the Newton's second law of motion. The trajectory of motion $x(t)$ will be called the classical trajectory.

The same transformations can be done for vectors $\vec{x}$ and $\vec{v} = d\vec{x}/dt$.

The function $-\frac{\partial U}{\partial x}$ is ordinary described as the sum of forces. Fortunately this function has a rather simple form.

A.8 Statistical mechanics

We have marked that the complete set of characteristics of the system can not be presented even for the simple systems. The account of the missed degrees of freedom or missed parameters can be made in a manner like it is done in statistical mechanics. Here one can use the derivation presented in [6]. Instead of precise characteristics $x_{i)}, v_{(i)}$ one has to use the distribution function ρ which is the probability P to find characteristic q in the interval $[q, q + dq]$ divided by dq

$$\rho(q)dq = P(q \in [q, q + dq])$$

When for H one can see

$$H = H_1 + H_2$$

where H_1 is the hamiltonian of the first group of particles and H_2 is the hamiltonian of the second group of particles then two subsystems are independent. It is shown directly from dynamic equation of motion. Then the distribution function $\rho(H)$ has to be the product $\rho(H_1)\rho(H_2)$

$$\rho(H_1 + H_2) = \rho(H_1)\rho(H_2)$$

The last functional equation has an evident solution

$$\rho \sim \exp(\beta H)$$

which determines the distribution function with a parameter β, which is proportional to inverse temperature.

Certainly, in foundations of the statistical mechanics it is necessary to see the hypothesis of Boltzman which states that the averaging over trajectory is equal to the averaging over ensemble. Rigorously speaking one has to prove this fact based on dynamic equations but it is very difficult to do.

Since the distribution has to be normalized

$$\int d\Gamma \rho(H) = 1$$

where $\int d\Gamma$ is the integration over all possible states, one can determine the normalizing constant b in expression

$$\rho = b \exp(-\beta H)$$

Then

$$b = [\int d\Gamma \exp(-\beta H)]^{-1}$$

One has to show that the missed coordinates do not change the functional form of the distribution function. Really, for $H = H_1 + aq^2$ we have

$$\rho(H) = \rho(H_1) \exp(-\beta a x^2)$$

and $\rho(H)$ differs from $\rho(H_1)$ only by the factor which coincides in the functional form with a normalizing factor.

The same derivations can be done for the arbitrary choice $x_l = b_j x_{(j)} + b_k x_{(k)}$ and the factors of the normal distribution appear.

The coordinates $v_{(i)}$ can be separated due to the form of H. This leads to the Maxwell distribution over velocities [6]

$$\rho(v_{(i)}) \sim \exp(-m v_{(i)}^2/2)$$

Summarizing this section we introduce the recipe to take into account the missed degrees of freedom by transition

- $$H \to \exp(-\beta H)$$

A.9 Simple solutions

The linear dependence of H does not lead to any progress. Now we shall present the solutions initiated by the simplest square form of H, i.e. $H = ax^2 + bv^2$. From the last section to have the convergence we see that constants a and b have to has the same sigh as $const$ in $H = const$. We have three possibilities

- $a = 0$

  Then $v = const$ and we have the straight uniform motion which is equivalent to the stationary state.

- $b = 0$

  Then $x = const$ and there is no motion. This case does not take place

- $a > 0, b > 0, const > 0$

  The solution is
  $$x = A \sin wt + B \cos wt$$
  where w is the frequency of oscillations.

The last case is the most common one. If instead of x_i we choose $x_{i+1} - x_i$, where x_i are coordinates of particles we get the moving wave which satisfies the wave equation

$$\frac{\partial^2 f}{\partial t^2} = \kappa \frac{\partial^2 f}{\partial x^2}$$

for a function f with a positive parameter κ.

A.10 Uncertainty relations

The base of the classical mechanics is in some sense contradictory. The value of velocity involved into the formalism of the classical mechanics is an ill defined value from the point of view of numerical methods. Really, the numerical definition of derivative

$$v = \lim_{\delta t \to 0} \frac{x(t + \delta t) - x(t)}{\delta t}$$

has a problems in calculation $\frac{x(t+\delta t)-x(t)}{\delta t}$ for small δt.

From a physical point of view of classical approach one can see that collisions with environment make the velocity of the Brownian particle a fluctuating value and the instant value of velocity can not be well determined while the coordinate of the Brownian particle is a stable characteristic.

These features require to consider some characteristic values of fluctuations δx and δv of x and v. The concrete form of uncertainty relation can be established on the base of quantum mechanics which is derived in next sections. Here one can stop the narration of this section.

These simple features show us that it is necessary to present some approach which has to take into account the impossibility to have in one and the same moment the value of x and v.

But also one can present some not so rigorous derivations leading to some interesting results. already the Liouville's theorem says that the volume in the phase space is conserved and, thus, $\delta p \delta x$ which is the elementary volume is conserved.

Analogous derivations following Hazen start from the Hamiltonian form of the law of motion

$$\frac{\partial H}{\partial p} = x' \ , \quad \frac{\partial H}{\partial x} = -p'$$

where a sign $'$ marks the derivative on time and an evident Maxwell relation $\frac{\partial^2 H}{\partial p \partial x} = \frac{\partial^2 H}{\partial x \partial p}$ and one can see that $\frac{\partial x'}{\partial x} + \frac{\partial p'}{\partial p} = 0$. Since for every function f $\frac{\partial f'}{\partial f} = \frac{f''}{f'}$ one can find $p'x'' + x'p'' = 0$ or $\frac{d}{dt}(p'x') = 0$. In terms of finite differences $\frac{d}{dt}(\delta p \delta x) = 0$ states that $\delta p \delta x$ remains some constant.

Now one can consider relation $\delta E \delta t$. certainly, the system following dynamic equations has $\delta E = 0$. Then one can not use here Hamiltonian relation but simply consider $E = E(x(t))$. Then $dE = \frac{dE}{dx}\frac{dx}{dt}dt$. Since $\frac{\partial E}{\partial x} = p'$ which can be regarded as a definition of momentum. Then $dE = p'x'dt$. Then $\delta E \delta t = p'x'dtdt = p'dtx'dt = \delta p \delta x = h$ where h is Planck's constant divided by 2π.

From the other point of view one can write $\delta \nu \delta T = 1$, where ν is a frequency, T is a period. Certainly $dT = dt$ and we see that $\delta E = h \delta \nu$. So, one can see that $E = h\nu$ since the shift in potential, i.e. in E is possible.

A.11 The amplitude of transition

It is necessary to give a theory for an elementary system which does not have fixed x, v. Since x is regarded as a main characteristic and v as additional we imply that at t_1 there is x_1 and at t_2 there is x_2. It is necessary to get an amplitude of such transition.

Since the system does not have fixed x, v one can not speak about the fixed point in the phase space but only about some probability to be in a fixed state in the phase space. We have already presented a transition from the fixed state to a distribution in a section devoted to statistical mechanics, but it is clear that this approach can not lead to a true result because in $\exp(-\beta H)$ the main role is played by the states with a minimal H. The less is the energy the greater is the weight of the state. In construction of the distribution for a separate system one can not use H and has to replace it by the characteristic of the system which has minimum on the classical trajectory. Rigorously speaking this characteristic S has to manifest three properties

- It attains minimum at the classical trajectory or somewhere near this trajectory
- It has to be an additive function of two non interacting parts of the whole system
$$S[1,2] = S[1] + S[2]$$
- It has to be an additive function of time
$$S(t_0, t_2) = S(t_0, t_1) + S(t_1, t_2)$$

The last two properties are necessary to consider $\exp(\alpha S)$ as some elementary probability or something connected with the probability. The first property ensures the correspondence between the classical theory and this approach.

Fortunately it is easy to present such characteristic

$$S(t_0, t_1) = \int_{t_0}^{t_1} (mv^2/2 - U(x))dt$$

The Euler equation for this functional coincides with equation of motion.

Then the amplitude K of transition can be presented as

$$K(a,b) = \sum_{\textit{All trajectories } x(t) \textit{ going from the state } a \textit{ to the state } b} \exp(\alpha S(a,b))$$

A.12 Classical limit

At first one has to see that the Euler equation for S is the classical equation of motion. The functional S can be written as

$$S = \int_{t_a}^{t_b} L(x, x', t)dt$$

where

$$L = mv^2/2 - U(x)$$

Having considered a variation of trajectory $x(t) \to x(t) + \delta x(t)$ we get

$$S(x + \delta x) = S(x) + \int [\delta x' \frac{\partial L}{\partial x'} + \delta x \frac{\partial L}{\partial x}]dt$$

To see this equation it is necessary to prove that x and x' are really independent variables but it i possible to do already in C^∞.

Then having integrated by parts and assuming that

$$\delta x \frac{\partial L}{\partial x'}|_{t_a} - \delta x \frac{\partial L}{\partial x'}|_{t_b} = 0$$

which is evident since x is fixed at t_a and t_b one can see that

$$\delta S = -\int \delta x [\frac{d}{dt}(\frac{\partial L}{\partial x'}) - \frac{\partial L}{\partial x}]$$

and due to the arbitrary variation δx one gets

$$[\frac{d}{dt}(\frac{\partial L}{\partial x'}) - \frac{\partial L}{\partial x}] = 0$$

at the minimum (maximum) of S. Since $L = mv^2/2 - U$ the last equation is reduced to

$$mx'' = -\frac{\partial U}{\partial x}$$

which is the classical equation of motion.

Now it is necessary to investigate the limit of this approach for macroscopic systems to show that the trajectory goes to the classical limit.

The approximately additive character of potential energy U and kinetic energy $\sum_i m_i v_i^2/2$ is very important for future analysis. Then the energy H and action S are the additive functions also.

For macroscopic objects the value of S is proportional to the number of particles N and, thus, the characteristic value of relative deviation Δx of trajectory from providing minimum is proportional to $N^{-1/2}$. It is very small and for macroscopic systems trajectory is the classical one.

A.13 Functional integral

The calculation of the amplitude

$$K(a,b) = \sum_{All\ trajectories\ x(t)\ going\ from\ the\ state\ a\ to\ the\ state\ b} \exp(\alpha S(a,b))$$

is rather difficult to fulfill and can be made by the formalism of the functional integration. Details can be found in [5]. For our purposes it is important that the integral

$$K(a,b) = \int \exp(\alpha S(a,b)) D[x]$$

where $D[x]$ is the infinite number of differentials in every point of trajectory or in other notations

$$K(a,b) = \int_{-\infty}^{\infty} \exp(\alpha S(a,b)) dx$$

is absolutely the same expression.

The formalism of the functional integral is well defined only in some special cases. One can restrict the class of trajectories, for example, consider the broken lines. This way requires the special limitations on trajectories which are not known. But for the special subintegral functions one has no need to make such restrictions. Namely, for the subintegral functions of the gaussian form

$$f \sim \exp(Square\ form\ of\ trajectory)$$

one can define the functional integral. The cause is the Pyphagorean theorem which allows to squeeze the number of differentials.

Fortunately, in the simplest cases of free dynamics (see the section "Simple cases") the function S is the square function of coordinates and the functional integral can be calculated.

One can see that the principle of squeezing coordinates is here the necessary condition to fulfill the calculations of the functional integral. Certainly here one has to observe a condition

$$Re(\alpha) \leq 0$$

if S is restricted from below.

A.14 Schrödinger equation

At first one can see the principle of superposition

$$K(b,a) = \int_{x_c} K(b,c)K(c,a)dx_c$$

where the integration is taken over all positions of trajectory at t_c.

This property allows to introduce some basic amplitudes $K(x_i,t_i;x_0,t_0)$ giving them a name "the wave function" $\psi(x_i,t_i)$. Then instead of

$$K(x_2,t_2;x_0,t_0) = \int_{-\infty}^{\infty} K(x_2,t_2;x_1,t_1)K(x_1,t_1;x_0,t_0)dx_1$$

we have

$$\psi(x_2,t_2) = \int_{-\infty}^{\infty} K(x_2,t_2;x_1,t_1)\psi(x_1,t_1)dx_1$$

Consider $S = \int_{t_0}^{t_1} L(x',x)dt$ for small intervals $\epsilon = |t_1 - t_0|$. Then

$$S = \epsilon L(\frac{x-y}{\epsilon}, \frac{x+y}{2})$$

where x is initial value of trajectory and y is the final value of trajectory. Then

$$\psi(x,t+\epsilon) = \int_{-\infty}^{\infty} \frac{1}{A}\exp(\epsilon\alpha L(\frac{x-y}{\epsilon}, \frac{x+y}{2}))\psi(y,t)dy$$

and $1/A$ is the normalizing factor.

Taking into account the explicit form of L one can get

$$\psi(x,t+\epsilon) = \int_{-\infty}^{\infty} \frac{1}{A}\exp(\alpha\frac{m(x-y)^2}{2\epsilon})\exp(\epsilon\alpha U(\frac{x+y}{2},t))\psi(y,t)dy$$

Having introduced $\eta = y - x$ one gets

$$\psi(x,t+\epsilon) = \int_{-\infty}^{\infty} \frac{1}{A}\exp(\alpha\frac{m\eta^2}{2\epsilon})\exp(\epsilon\alpha U(x+\eta/2,t))\psi(x+\eta,t)d\eta$$

Now one can decompose ψ in powers of ϵ and get

$$\psi(x,t) + \epsilon\frac{\partial\psi(x,t)}{\partial t} = \int_{-\infty}^{\infty} \frac{1}{A}\exp(\alpha\frac{m\eta^2}{2\epsilon})(1+\alpha\epsilon U(x+\eta/2,t))\psi(x+\eta,t)d\eta$$

One can see that for

$$2\epsilon\alpha m \sim \eta^2$$

the characteristic cancellation takes place and, thus, η has also some smallness. So, it is necessary to decompose in powers of η which gives

$$\psi(x,t)+\epsilon\frac{\partial\psi(x,t)}{\partial t}=\int_{-\infty}^{\infty}\frac{1}{A}\exp(\alpha\frac{m\eta^2}{2\epsilon})(1+\alpha\epsilon U(x+\eta/2,t))[\psi(x,t)+\eta\frac{\partial\psi}{\partial x}+\frac{1}{2}\eta^2\frac{\partial^2\psi}{\partial x^2}]d\eta$$

and

$$\psi(x,t)+\epsilon\frac{\partial\psi(x,t)}{\partial t}=\int_{-\infty}^{\infty}\frac{1}{A}\exp(\alpha\frac{m\eta^2}{2\epsilon})(1+\alpha\epsilon U(x,t))[\psi(x,t)+\eta\frac{\partial\psi}{\partial x}+\frac{1}{2}\eta^2\frac{\partial^2\psi}{\partial x^2}]d\eta$$

In the zero order

$$\psi(x,t)=\int_{-\infty}^{\infty}\frac{1}{A}\exp(\alpha\frac{m\eta^2}{2\epsilon})d\eta\psi(x,t)$$

and then

$$A=(\frac{-2\pi\epsilon}{m\alpha})^{1/2}$$

Having calculated integrals one gets

$$\frac{\partial\psi}{\partial t}=A\psi+B\frac{\partial^2\psi}{\partial x^2}$$

with $|A|=|\alpha U|$, $|B|=|1/(2\alpha m)|$ which is the Shrödinger equation. So, the dynamic equation of quantum mechanics is derived.

This derivation reproduces the analysis presented in [5] but for an arbitrary parameter α. Now the task is to determine α.

The value of α can be determined by the fact that in squeezed dimensions the classical solution and the solution of Shrödinger equation must have one and the same form because there is absolutely no information what theory has to be applied. Classical and quantum approaches have to coincide in the parts where nothing is known about the system.

The classical approach gives the solution in the case when nothing is known - this solution is described in the section "Simple solutions". We know this solution - in classical approach this is the superposition of oscillations or waves. So, quantum approach has to lead to the same waves and oscillations, at least in their functional form. So, α has a purely imaginary magnitude

$$\alpha=\sim i$$

A.15 Sense of the wave function

Having derived the dynamic equations one has to clarify the sense of the amplitude K or at least the wave function ψ. It is clear that these objects have to be connected with a probability. So, when we have quantum objects with the wave function ψ in coordinate representation, i.e. as the function of coordinate x, we have the density $n(x)$ as the probability Pdx to have a particle into interval $[x, x+dx]$ as some function F of ψ

$$n(x) = F(\psi(x))$$

One have to specify this function F and it can be done from some evident requirements coming from constructions of continuous (field) models. Certainly, quantum approach has to allow constructions of continuous models at least to construct the field theory. Then it is necessary to fulfill the averaging over all wave functions ψ. In statistical mechanics construction it is also necessary to average over all states, i.e. over all wave functions. (Here there is no necessity to consider restrictions to occupy one and the same energetic level for different states providing different statistics, one can simply forget about them.) So, the formalism of the functional integration naturally appears here. The function to be averaged looks like $\exp(G)$ where G is proportional to H, S or some other similar function. For us it is only essential that there will be potential energy U which is included into these functions. Potential energy U has to be written via the density n as

$$U = \int_{-\infty}^{\infty} u(x)n(x)dx$$

Then it is necessary to fulfill the functional integration

$$\int \exp(\alpha \int_{-\infty}^{\infty} u(x)n(x)dx)D[\psi]$$

with some constant α.

We do not know the real number of coordinates in $D[\psi]$. So, the required functional integration can be fulfilled only when the argument of exp has the gaussian form. Then it is necessary that

$$n(x) \sim \psi^2$$

The value of n has to be a real number which requires to have a real number in the rhs of the previous relation

$$n(x) \sim |\psi|^2$$

Alternative possibility is to take $(Re\psi)^2$ which gives a hardly appropriate result of a quickly oscillating function.

One can see that here again the Pyphagorean theorem plays the fundamental role and the squeezing principle works to determine the sense of ψ.

Having recalled that n is proportional to the probability we see that the wave function has a simple physical meaning: $|\psi|^2$ is the differential probability to find a quantum object in an elementary interval near x.

A.16 Procedure of measuring

Procedure of measuring is certainly the interaction between the quantum object under investigation and the macroscopic object giving the result of measuring. One has to realize that it is impossible to give the detailed theory of such interaction and certainly every type of measurements has its own particular features and, thus, the detailed theory describing the measurements. But one can come to the main features of the measuring procedure already from the general principles neglecting the concrete picture of interaction between the quantum particle and the classical object.

Let us speak about the quantum particle and the measuring device. The action of the device will be described by an operator A. The elementary interaction between the particle and the device will be presented by application of an operator A to a wave function ψ. Since operator A is an arbitrary one, here no supposition is made. When we speak about the additive character then it is reasonable to take A as a linear operator. The process of interaction between the particle and the device can not be controlled - one can not say how many times the particle interacts with the device. So, the final state has to be stable - the next application of A does not essentially violates the wave function. Then it is necessary that

$$A\psi_{final} \sim \psi_{final}$$

Then ψ_{final} is an eigenfunction of A.

The evident physical reason of such requirement is the observation of only resonances. It is known that the problem of eigenfunctions appears in classical mechanics when the resonances of oscillating systems are investigated. From other side the resonances are the most clear observed peculiarities of the system and there is absolutely nothing strange that namely resonances are considered as the observable features while all other features are neglected.

It is known that a linear operator A has many eigenfunctions. What eigenfunction will be taken here? Now it is necessary to decide with what intensity (probability) the result of measuring is some ψ_i

$$A_i\psi_i = a_i\psi_i$$

where a_i is an eigenvalue.

We see that for the macroscopic flow of particles with wave functions ψ (it will be marked as Ψ) the result will be α_i functions ψ_i . Here α_i are some stable characteristics.

After the procedure of measurement we have instead of Ψ the sum $\sum_i \alpha_i\psi_i$.

$$\Psi \to \sum_i \alpha_i\psi_i$$

At first there is no requirement that there is an equality between Ψ and $\sum_i \alpha_i\psi_i$. But if we make a measurement by operator A of the characteristic a, then by operator B of characteristic b, etc, then it is necessary that the next measurement does not feel the previous one. For unique particle this is not true, but for macroscopic flow this has to be observed, certainly, at the imaginary level. We do not know who at when makes observations. But we have to adopt that somebody very curious makes this observation without any traces. Then we have to have to possibility to ignore this observation.

The recipe of observation has to be one and the same for every observation. It can not depend on the previous observation.

To exclude the influence of the previous observation for the macroscopic flow we need a linear law of reconstruction Ψ on a base of ψ_i. Then Ψ has to be reconstructed as a linear combination of ψ_i. Then

$$\Psi = \sum_i b_i\psi_i$$

and b_i are coefficients in decomposition. Then since $|\psi|^2$ is the probability one can see that $|\alpha_i|^2$ are the probabilities to get Ψ_i and the result a_i of the measurement. Then $\alpha_i = a_i = b_i$.

As the result we see that the necessary features of observation can be established without detailed description of interaction. Certainly, to fulfill the requirements of real eigenvalues and completeness the operators A have to be self-adjoint ones in a corresponding space.

A.17 Conclusions

In this review all constructions are based on the conception of the measurements. At first it is introduced in classical mechanics. Then the quantum mechanics is regarded as some regularization of equations appeared in classical mechanics. This way is used in other branches of science, certainly one can consider the equations of hydrodynamics as some very advanced way to make the equations of motion more stable. Here the same idea is used.

All conclusions made above have to be checked many times before they can be regarded as reliable features of mechanics. But even now it is clear that attempts to build a primitive physical model for every phenomenon in nature and consider it as the absolute truth has an evident error in its foundation.

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